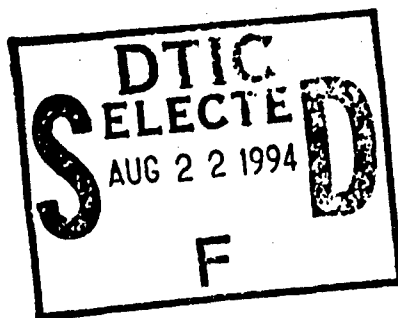


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MIGRATION OF ENERGY

By V. N. Tarusov

- USSR -

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MIGRATION OF ENERGY

[Following is a translation of an article by V. N. Tarusov in the book Osnovy Biofiziki i Biofizicheskoy Khimii (Fundamentals of Biophysics and Biophysical Chemistry), Part I, Moscow, 1960, pp 26-39]

In a study of the luminescence of crystals, it was found that deexcitation may occur, not at the place and in the atom where the photon struck, but at some distance. This phenomenon is observed when there are impurities, even very negligible, in the crystal. For example, luminescence occurs under the influence of radioactive emissions on crystals of zinc sulfide containing copper as an impurity in amounts of 0.01%. A spectral investigation shows that the copper atoms luminesce exclusively. The amount of energy obtained by the crystal is almost completely deexcited by the copper atoms, although the overwhelming amount of the energy is absorbed by the zinc and sulfur atoms. These experiments show that the zinc and sulfur atoms are capable of absorbing radiant energy and transferring it almost without loss to the copper atoms, sparsely distributed in the crystal lattice. Such a phenomenon has also been detected in other crystals and even in noncrystalline systems.

A characteristic feature of this phenomenon proves to be the fact that the migration of the electron occurs at great distances, from the molecular point of view. When an electron is moved from the atom that absorbed the quantum to the emitting atom, it must cover a space extending up to 50 Å and avoid most of the atoms. It is characteristic that the electron possesses an affinity precisely for the fluorescing atoms, and does not expend its energy while completing this complex journey.

The mechanism of this phenomenon is explained by the structural peculiarities of the crystals. In the crystal lattice there are electrons that are components not of each given atom, but are general components of the entire crystal. In crystals possessing electron conduction, according to the quantum conditions, bands with various energy levels are formed, which are filled with electrons. Part of the level may remain unfilled in this case. When a quantum of energy is absorbed in the basic lattice of the crystal, an electron from an occupied band passes into an unoccupied band, migrates along it, and,

giving off its energy, goes down to a lower level. The empty place remaining in the band B is filled by one of the electrons from another band C (Fig. 3).

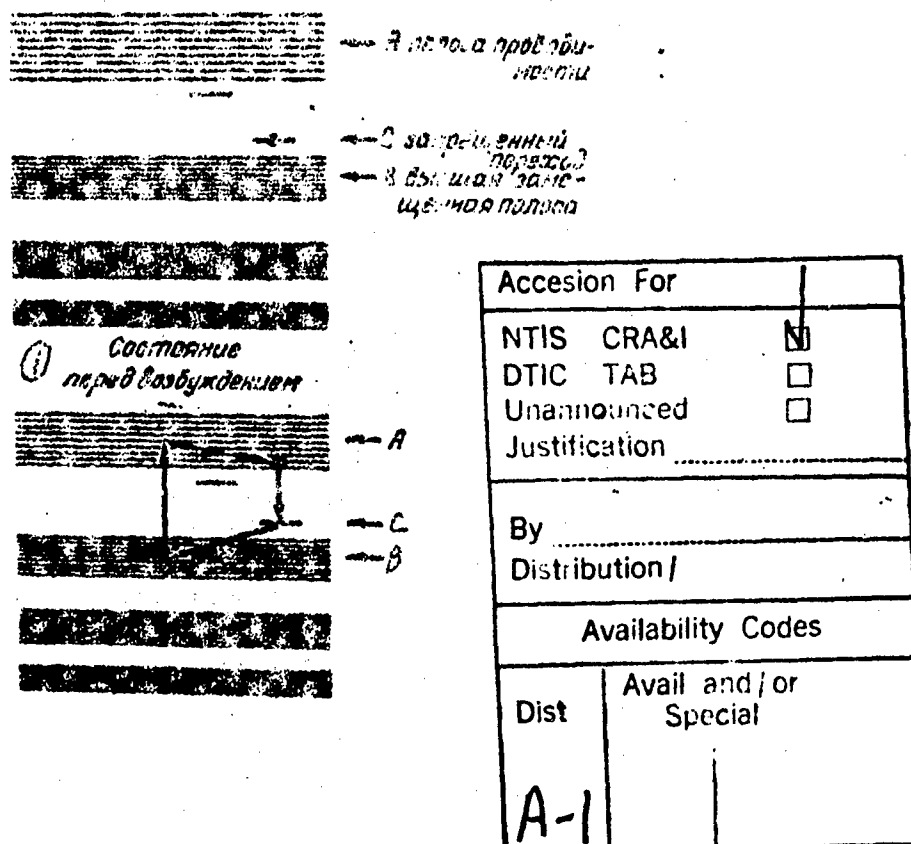


Fig. 3. Scheme of migration of electrons in crystals (Riehl).

A -- conduction band; B -- higher substituted band; C -- forbidden transition; 1 -- state before excitation.

The theory has been advanced that the migration of energy may also occur without direct migration of electrons. Frenkel (1936) has indicated that if any atom in the molecule is found in a state of excitation, this excitation can be inductively transferred to other atoms and can move until it reaches an atom in which a reaction arises under the influence of the excitation. Spectral investigations have established that if hydrocarbon chains contain double bonds, separated from one another by several ordinary bonds (Fig. 4), then when energy is absorbed the absorption bands do not change their position. In chains containing so-called conjugated bonds, i.e. double bonds separated from one another by only one ordinary bond, a lengthening of the wave occurs. This shows that in such a system the double bond

exists in an energetic interaction with the other double bonds, and that the energy absorbed by one bond is also distributed to the other bonds. It is proposed that such a nature of the bond can exist only in living protein, and that there are none of them in dead protein.

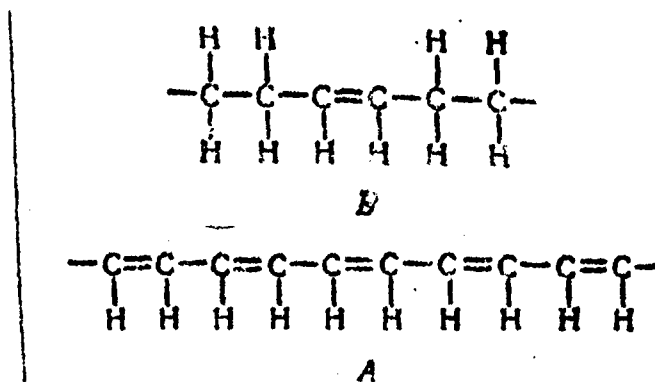
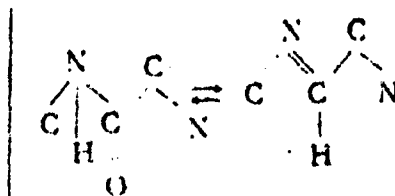


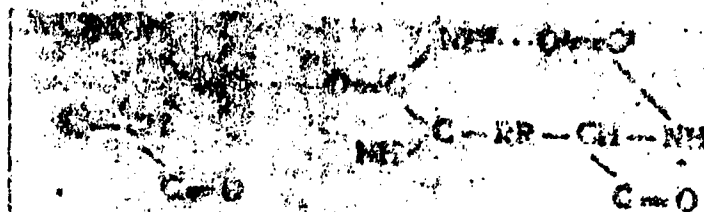
Fig. 4. Conjugated bonds. A -- system with conjugated bonds; B -- system with unconjugated bonds.

On the basis of these observations, a hypothesis has been advanced (Schmidt, 1947) that a conjugated bond arises along the peptide chain of a protein molecule as a result of the tautomeric transition



However, there were no experimental evidences in favor of this theory.

Considerable difficulties were also encountered by the theory of the possibility of migration of electrons across the peptide bonds of protein (Evans, Gergely, 1949). The possibility of delocalization of π -electrons was postulated on the basis of X-ray structural analysis and quantum mechanical calculations. In view of this, it is considered as proven that the π -electrons of nitrogen and CO can be displaced



This interesting proposal is speculative in nature.

One of the most urgent problems of modern biophysics is the problem of whether migration of energy occurs during biological processes and with the aid of what mechanisms it is accomplished: as a result of the transfer of electrons, as a result of resonance phenomena or vibration processes? The high efficiency of certain processes that take place in living systems might be explained by migration of energy.

The decomposition of adenosine triphosphoric acid (ATP), as is well known, gives the energy for shortening the myosin threads. Szent-Gyorgy (1956) advanced the hypothesis that centers in which decomposition of ATP occurs are not found in each myosin fiber. At the same time we know that all the fibrils are shortened, and there are less centers than fibrils. The shortening of the fibrils occurs in a very short time; hence we cannot assume that the energy is transferred by diffusion means. The hypothesis arose that in this case the transfer of energy occurs on account of the limit of electronic excitation of the electrons, just as in phenomena of fluorescence in crystals.

Extremely interesting data have also been obtained (Richer, Kasperson, 1946) in a study of the energetics of the cytochromes, which perform the oxidation of hydrogen, and as a result play a vital role in the oxidative processes that take place in the cells. The cytochromes contain iron in the di- and trivalent form, where one form is constantly being converted to the other. Structurally the cytochrome represents a large protein molecule, on the periphery of which an iron-containing group is situated. The molecular weight of cytochrome is of the order of several hundred thousands. Attempts have been made to link the mechanism of the oxidation and reduction of iron to the structural peculiarities of the cytochrome. In order for the transfer of oxygen from one atom of iron to another to be possible, these atoms of iron should be situated one opposite the other. In the presence of more than two atoms of iron, such a distribution is impossible. If there are more than two molecules of cytochrome, then any of them should adjoin each other not with iron atoms, but with their protein portions. In view of this, the hypothesis was advanced that the energy is transferred between iron atoms along a protein bridge.

As a second example we might cite the investigation of myoglobin conducted by Bucher and Kasperson. Myoglobin is bonded to four molecules of CO. This compound decomposes under the action of light. The myoglobin molecule consists of an inert protein nucleus and a hemin group, which is bonded to the CO. The absorption spectra of the protein nucleus and hemin group are different. The protein nucleus has an absorption maximum in the UV region, due to tyrosine and tryptophan; the hemin group has a maximum in the region of 400-500 Å.

Bucher and Kasperson determined the amount of CO split out by irradiating myoglobin with various parts of the spectrum in the region of 2800-5000 Å at equal amounts of energy. They established that the amount of CO split out both in irradiation by light with a wave length of 2800 Å and in irradiation by light with a wave length of 5000 Å was the same, in spite of the fact that in the first case the absorption of energy occurred in the protein portion of the myoglobin molecule, while in the second case it occurred in the hemin group. This phenomenon can be explained by the fact that splitting out of an electron occurs in the protein molecule under irradiation by ultraviolet; the electron migrates along the protein to the hemin group, where reduction of iron takes place. The comparatively low quantum yield of this reaction, less than 20%, gave a basis for objections (Terenin, Krasnovskiy, 1949) that in this case the transfer of energy could have occurred thermally, and that heating could have led to thermal dissociation of the CO of myoglobin.

However, taking into consideration the fact that according to the calculations, the heating in this case is very small, no more than 1%, the experiments of Bucher and Kasperson can still be considered convincing.

Now the question of the possibility of migration of energy in protein is being vigorously debated. The experiments of Bannister (1954), who used the natural chromoprotein pigment, phycocyanin, in which eight to 16 molecules of the chromophore are bonded to a molecule of globulin, as evidence for this theory, have obtained widespread recognition. The author obtained a rather high quantum yield -- almost half the energy, where the possibility of thermal transfer of energy was excluded. A determination of the absorption maximum of the pigment phycocyanin itself showed that this maximum lies in the region of 350-400 and 615 Å, while that of the protein (the determination was performed in hydrolysates) lies at 275 Å.

Experiments have shown that the quantum yield was the same, independent of the spectral region of the source of excitation. Although Bannister's experiments evoked many objections, in particular in connection with the fact that the determination of the absorption maximum of the protein was performed not with the native protein, but with a hydrolysate, these experiments give a basis for assuming that the migration of energy proceeds along protein bridges. In any case, the absorption spectrum of the protein determined by Bannister could not differ greatly from the true spectrum, since the spectral

absorption of the protein is due to amino acids, chiefly tyrosine and tryptophan, which remained undecomposed in the hydrolysate.

This phenomenon has been clearly demonstrated in the experiments of French and Joung (1952) with red algae, in which there are three pigments: chlorophyll, phycoerythrin, and phycocyanin. The absorption region of chlorophyll is 400-450 \AA , that of phycoerythrin 450-550 \AA , and that of phycocyanin -- with a maximum at about 620 \AA . It was established that fluorescence of chlorophyll is obtained with a high quantum yield when the system is irradiated with light with a wave length of about 450 \AA , which is absorbed by phycoerythrin. At the same time, fluorescence of phycocyanin occurs. This shows that chlorophyll and phycocyanin obtain energy from the phycoerythrin, which can be accomplished only by means of migration of energy (Fig. 5).

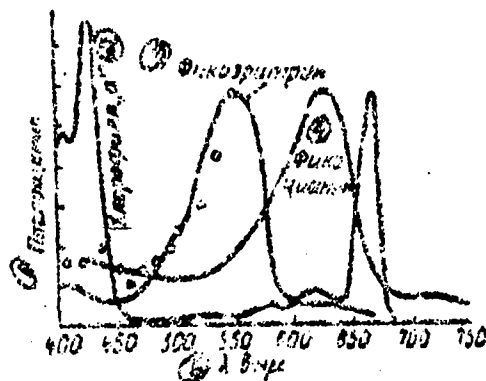


Fig. 5. Effectiveness of excitation of fluorescence of chlorophyll (French, Joung).

1 -- absorption; 2 -- chlorophyll "a"; 3 -- phycoerythrin; 4 -- phycocyanin; 5 -- λ in $m\mu$.

Analogous data have been obtained on the alga *Chroococcum* and on purple bacteria, where a transfer of energy was observed from the pigments that absorb short waves to the pigments that absorb long waves.

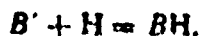
The question of the prevalence of this process in biological systems and of the mechanism of such a migration remains debatable. Terenin and Krasnovskiy (1949) believe that the transfer of electrons along protein bridges is impossible, and that, most probably, migration of energy occurs vibrationally along chains of molecules.

The fact that hemin itself does not possess the ability to fluoresce is advanced as an objection to the possibility of migration of energy in myoglobin.

Attempts at broader generalizations have also been made to explain the phenomenon of migration of energy in a number of biological processes. Thus, the hypothesis has been advanced that under the action of enzymes a transfer of energy at a distance without any dispersion of it always occurs. According to this theory, the transfer of energy in dehydrogenase and redoxase is accomplished according to the following scheme: for example, A -- hydrogen donor, B -- hydrogen acceptor. The first step of the transfer is the splitting of the compound AH into ions: $AH = A + H$. In order for B to enter into a compound with H, B should obtain a negative charge. This charge -- a migrating electron -- passes from A to B.



After this B adds H:



For example, in a protein (Fig. 6) molecules A and B are situated at a considerable distance from one another (at a distance of tens of molecular radii). The protein layer is surrounded by water, dissociated into H and OH ions. A splits out an electron and acquires a positive charge, while H is split out into the aqueous medium as a result. The electron migrates along a bridge to B; B acquires a negative charge, and as a result seizes a hydrogen from the external medium. There is no direct transfer of the hydrogen ion; the reaction is accomplished by transfer of an electron.

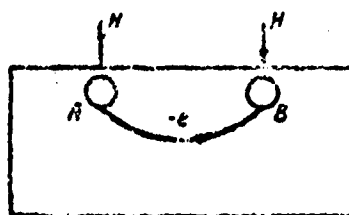


Fig. 6. Scheme of migration of an electron under the action of dehydrogenase.

At present there are a number of points of view on the possible mechanism of the migration of energy in proteins. As has already been indicated above, the electronic type of energy migration is possible in crystal structures where free conduction bands exist. The presence of free conduction bands is usually detected by an increase in the electroconductivity under the appropriate influence (irradia-

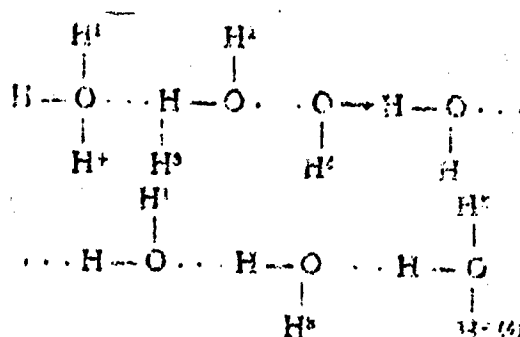
tion). In view of this, experiments in which it was possible to detect an increase in the electroconductivity when protein was irradiated, have been conducted to demonstrate the possibility of migration of energy in protein. Thus, for example, in the light Szent-Gyorgy (1956) detected an increase in the electroconductivity of gelatin to which pigment systems have been added. However, he did not demonstrate that such an effect might be due only to the pigment.

A negligible increase in the electroconductivity was also found in uncolored gelatin (Riehl, 1955), which might possibly be due to impurities. We should consider in this case the fact that gelatin, although a protein, differs greatly from native proteins in its structure and properties.

Many researchers (Terenin, Krasnovskiy, 1949) consider the electronic type of energy migration in proteins as relatively improbable, due to the absence of any crystal structure in them.

In addition to the possibility of migration of energy by means of electrons, the hypothesis has been advanced that such a migration may be accomplished on account of motion of protons.

On the basis of his investigations of energy migration in ice, Riehl advanced the hypothesis that the same type of migration of energy can also occur in proteins. In this case the proton conductor may be solvated water on the surface of the protein molecules, which, as is well known, possesses the properties of ice. The role of the factor creating an ordered structure, according to this hypothesis, is played by the polypeptide chains of the proteins, to which the water is connected by means of hydrogen bonds. According to this scheme, if the formation of an ion pair OH^- and H^+ occurs in any section, the proton in the oxonium ion passes to the neighboring molecule:



Certain researchers (Vladimirov, Konev, 1957) believe that the most probable mechanism of the migration of energy in protein systems is a resonance mechanism, which was proposed by Davila and Perren to explain the migration of energy between dimolecules. In this case a crystal structure is not required; it is necessary only

that the energy donor possess fluorescence, the spectrum of which overlaps with the absorption spectrum of the acceptor, and that the donor be no more than 100 Å away from the acceptor.

These conditions, in the opinion of the authors indicated above, are satisfied in proteins. For example, amino acids absorbed on paper possess fluorescence, and the spectra of amino acids and proteins overlap on mass, as is shown by many investigations (Weber, 1953; Dannister, 1954; Schore, Perdee, 1956). The opinion exists (Schmidt, 1947) that the hydrogen bonds that create the double bond in amide chains are the resonating system of the protein molecule.

There are a number of experimental facts in favor of the concept of a resonance mechanism of the migration of energy in protein. Investigations of the migration of energy on phycoerythrin (Konev, 1957) have shown that heating of the system to 80°, leading to denaturation of the protein, does not disrupt the mechanism of the energy transfer. In the case of electron transfer, denaturation should have disrupted the migration process, since in this case the structure of the protein, which is a necessary condition for electronic migration (the existence of a conduction zone), is disrupted. However, in native proteins both types of energy migration are apparently possible. It has been found, for example (Konev, 1957; Vladimirov, Konev, 1957), that there are two fluorescence maxima in native proteins under excitation by visible light -- in the region of 280 Å and in the region of 240 Å. The first maximum did not disappear after denaturation. The second maximum, which was observed only in native proteins, disappears under the influence of heat and other denaturing agents (urea, pH). On the basis of this the authors make the quite correct assumption that the transfer of energy in the second maximum is related to the structural organization of the protein and assume that in this system the transfer of energy takes place through the electrons according to the zone conduction type. Work with paramagnetic resonance also supports the theory that such conduction bands can exist in protein. With the aid of this method, Blyumenfel'd and Kal'manson (1957) detected maxima belonging to free delocalized electrons in amino acids. Analogous maxima have been found by this same method in native proteins (Commoner, Heise, 1957).

The hypothesis of the possibility of electronic migration of energy during the conduction of a nerve impulse (Riehl) is based on purely external analogies. However, we cannot but consider the fact that when a cell passes into a state of excitation during the passage of an impulse along a nerve, structuring and polymerization occur, leading to the formation of threadlike reversible structures, along which migration of energy might be accomplished. The possibility of electronic transfer in this case is doubtful, since numerous experiments of various authors have shown that a magnetic field does not influence this process.

Views are expressed that the migration of energy by electrons plays a vital role in the process of photosynthesis. In an analysis

of the kinetics of the photosynthetic process, it has been established that this process is made up of two successive reactions, the first of which develops at the moment of irradiation, while the second takes place after the illumination has ceased (Blaug's dark reaction). In work with an intermittent pulse illumination, it was established that the maximum effectiveness of photosynthesis is achieved at a definite ratio of the periods of illumination and darkness. The investigation of these relationships led to the conclusion that the chlorophyll molecule is considerably larger than the point in which the dark reaction takes place. One "dark" point accounts for an average of up to 2000 molecules of chlorophyll, which supply energy to these points. Calculations have shown that such a number of chlorophyll molecules cannot be distributed around the dark point where the chemical reaction takes place in such a way that all the molecules are directly in contact with it. Nor can a distribution of the chlorophyll molecules in several layers guarantee a transfer of energy, since the migration of energy in chlorophyll does not occur, in connection with the fact that there are no free conduction bands in chlorophyll. A satisfactory model explaining the possibility of energy migration from the chlorophyll molecules to the dark points was created on the basis of morphological data even before the question of migration of energy arose. In this scheme a protein bridge plays the role of a conduction band. An electron from the chlorophyll molecules moves along this bridge to the center where the chemical reaction is accomplished. It is not yet clear how migration of energy is accomplished in this bridge. Possibly the transfer of energy is accomplished in a way analogous to that proposed by Frenkel in the exciton theory. Frenkel proposed that the transfer of energy is accomplished by a successive transition of the molecule into a state of excitation or by means of vibration. An experimental approach to solving this problem is difficult; hence, this theory is as yet speculative in nature. A great role here should be played by investigations of pigments in vivo (Litvin, 1958). Interesting data have been obtained in experiments on the alga *Chroococcus* (Arnold, Oppenheimer, 1950), which has two pigments -- chlorophyll and phycocyanin, the spectral absorption regions of which lie far from one another. The maximum for chlorophyll lies in the region of 6800 Å, that for phycocyanin in the region of 4000 Å. Experimental investigations show that in irradiation by the portion of the spectrum that is absorbed by phycocyanin, and by that which is absorbed by chlorophyll, the quantum yield proves to be the same. Photosynthesis can be accomplished only by chlorophyll. In the irradiation of phycocyanin, the electrons apparently migrate from the phycocyanin molecules to the chlorophyll molecules, as a result of which photosynthesis is accomplished.

One of the facts advanced in favor of the theory of migration of energy was discovered in a study of the quantitative principles of the production of mutations. In an investigation of the dependence

of the appearance of mutations on the dose of X-rays (Riehl, Rompe, Timofeev-Resovsky, 1943), it was established that mutation can be obtained after influence on even one or several atoms. Calculating the volume in which the incidence of the photon should occur (i.e. the probability of appearance of a mutation caused by radiation), they found that

$$N = 1 - e^{-pza/A}$$

where a is the number of atoms in the section of incidence; A is the number of atoms in 1 cm^3 ; p is the "efficiency"; z is the number of ionizations in 1 cm^3 .

Determining the value of A on the basis of experimental data, the authors showed that the smallest volume of incidence was many times (approximately 1000 times) greater than the volume occupied by the molecules that react to the incidence of the photon. Certain authors attempt to explain this effect of migration of energy in the mutation process by diffusion of water radicals, formed in the irradiation (Zirkle, Tobiasch, 1953).

Speaking of the possibility of migration of energy in biological systems, we must take into consideration the fact that there are vast differences between model experiments on proteins and actual physicochemical conditions. Investigations of the physicochemical state of living protein show that it possesses some sort of labile bonds and structure that are not at all reproduced by proteins isolated from the cells. It is well known that structuring of protoplasm takes place under excitation and upon transition to the active state. It is converted to a gel, and fibrillar structures are detected in it. This should create favorable conditions for the migration of energy. It was described long ago that under irritation and the initial stages of necrosis, protoplasm acquires the ability to luminesce.

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